MODELLING AND ENVIRONMENTAL ASSESSMENT OF HETEROGENEOUS CATALYSIS BIODIESEL PROCESS USING WAR ALGORITHM

AS ELEYANA BINTI ALI

Thesis submitted in fulfillment of the requirements
for the award of the degree of
Bachelor of Chemical Engineering

Faculty of Chemical and Natural Resources Engineering
UNIVERSITI MALAYSIA PAHANG

FEBRUARY 2013

MODELLING AND ENVIRONMENTAL ASSESSMENT OF HETEROGENEOUS CATALYSIS BIODIESEL PROCESS USING WAR ALGORITHM

ABSTRACT

Environmental assessment in a preliminary designing stage of a process is important to evaluate the environmental friendliness of a process design, minimizing the environmental impact of the process. WAR algorithm, a methodology for determining the potential environmental impact (PEI) of a chemical process is developed to describe the flow and the generation of PEI through a chemical process. WAR algorithm which acts as a comparison tool in selecting the environmentally benign design option is developed using heterogeneous catalysis and alkali homogeneous catalysis of biodiesel process as case study. Heterogeneous catalysis of biodiesel process flowsheeting is first developed and simulated using Aspen Plus 7.0. Data and simulation results are then exported to the spreadsheet for environmental assessment of WAR algorithm. Four PEI indexes (TRO,TOP,TRG,TGP) are used to evaluate the environmental friendliness of a process design while eight PEI categories (four global and four toxilogical) are used to evaluate the PEI indexes. Comparison of the PEI indexes concluded that heterogeneous catalysis of biodiesel process showed more environmentally friendly process with minimum amount of PEI value compared to homogeneous catalysis process.

PENILAIAN ALAM SEKITAR TERHADAP PEMPROSESAN BIODIESEL MELALUI PEMANGKIN HETERO MENGGUNAKAN KAEDAH WAR ALGORITMA

ABSTRAK

Penilaian Alam Sekitar di peringkat awal rekabentuk proses adalah penting untuk menilai tahap mesra alam sesuatu reka bentuk proses, mengurangkan kesan alam sekitar disebabkan proses tersebut. WAR algoritma, kaedah untuk mengenalpasti potensi impak alam sekitar (PEI) sesuatu proses kimia, dirangka untuk menerangkan aliran dan penghasilan PEI di dalam proses. WAR algoritma yang bertindak sebagai alat perbandingan dalam memilih reka bentuk pilihan yang mesra alam dibangunkan dengan menggunakan proses penghasilan biodiesel menggunakan pemangkin heterogen dan pemangkin homogen alkali sebagai kajian kes. Rangka proses penghasilan biodiesel menggunakan pemangkin heterogen dirangka dan disimulasi menggunakan Aspen Plus 7.0. Data dan keputusan simulasi kemudiannya dieksport ke spreadsheet untuk penilaian alam sekitar menggunakan kaedah WAR algoritma. Empat PEI indeks (TRO, TOP, TRG, TGP) digunakan untuk menilai keramahan alam sekitar rekabentuk proses manakala lapan kategori PEI (empat global dan empat toxilogical) digunakan untuk menilai indeks PEI. Perbandingan indeks PEI menyimpulkan bahawa pemangkinan heterogen proses biodiesel menunjukkan proses yang lebih mesra alam dengan jumlah nilai PEI yang minimum berbanding dengan proses penghasilan biodiesel menggunakan pemangkin homogen.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

AP	Acidification Potential
ASTM	The American Society For Testing and Material
ATP	Aquatic Toxicity Potential
$C_{19}H_{36}O_2$	Methyl Oleate
$C_3H_8O_3$	Glycerol
$C_{57}H_{104}O_6$	Triolein
CH_4O	Methanol
FAME	Fatty Acid Methyl Ester
GWP	Global Warning Potential
H_2O	Water
HTPE	Human Toxicity Potential by Inhalation/ Dermal Exposure
HTPI	Human Toxicity Potential by Ingestion
ODP	Ozone Depletion Potential
PCOP	Photochemical Oxidation Potential
PEI	Potential Environmental Impact
PFD	Process Flow Diagram
TGP	Total Rate Generation/Product
TGR	Total Rate Generation
TOP	Total Rate Output/Product
TRO	Total Rate Output
TTP	Terrestrial Toxicity Potential
WAR	Waste reduction algorithm

LIST OF APPENDICES

CHAPTER 1

INTRODUCTION

1.1 Background of Study

Biodiesel is the name given to a clean burning mono-alkyl ester based oxygenated fuel made derived from renewable lipid feedstock such as vegetable oil or animal fat. Biodiesel is normally derived using catalyzed transesterification reaction in which the renewable lipid feedstock reacts with alcohol (Zhang *et al.*, 2002). Homogeneous acid and alkali process design are conventional methods that are widely used in industry. However, heterogeneous catalysis and supercritical methanol process have been reviewed to show advantageous over the conventional process.

West *et al.*, (2008), reviewed on methods to reduce the production cost of biodiesel which is first by replacing the virgin oil feedstock with a waste cooking oil feedstock. The second method is by the uses of solid catalyst replacing the rely on homogeneous catalyst which consume energy, time and cost due to the purification step of catalyst. Both methods can be achieved using heterogenous catalysis biodiesel process. The third method is by the uses of alcohol in its supercritical state and eliminates the need for catalyst. Based on his study which compared the feasibility of homogenous, heterogenous, and supercritical methanol process, heterogeneous catalysis process had showed advantageous over the other process. Thus, the production of biodiesel from waste cooking oil based on continuous heterogeneous catalysis process is used as a case study and model for the simulation and environmental assessment in this study.

In this study, pollution prevention technique is incorporated into the biodiesel process design by determining the flow and generation of potential environmental impact (PEI) through the process using WAR algorithm method. In process design stage, environmental assessment or pollution prevention is normally not taking into consideration as economics, operating and capital issue predominant the entire design. Method of WAR algorithm is used in evaluating the relative environmental impact of chemical process. It is a methodology that are considered only during the manufacturing level of chemical process which is therefore suitable to be used during the design stage of new process or for the modification of the existent process. Besides, it adopts simple algorithms and parameters which are therefore suitably used in accessing the environmental performance of biodiesel design in this study.

1.2 Problem Statement

Economics assessment, operating and capital design were the predominant issue in process design stage while environmental assessment was rarely introduced in a process design. Environmental concern received more attention in recent years thus implementing environmental assessment is an advantage in process design.

In environmental assessment of process design, common environmental performance used was LCA which was time consuming and costly. Alternatively, WAR algorithm was used as it is best performed during designing stage due to the simpler approaches it have. (Othman, 2011). Environmental assessment using WAR algorithm method determined the potential environmental impact (PEI) through a process thus help to evaluate the effect that the mass and energy of the process would have on the environment if they were to be emitted to the environment.

1.3 Objectives

The objectives of this thesis are to simulate the process flowsheet of heterogeneous biodiesel production using Aspen Plus Simulator and carry out the environmental analysis of the process using WAR Algorithm.

1.4 Scope of Study

In this study, continuous process of biodiesel production at a rate of 8000 tonnes/year using heterogeneous catalyst is modeled and simulated based on the design and parameters referred from West (2007). Results from simulation are then used to perform economic and environmental analysis. The scopes of this study include:

i. Simulate the continuous process flowsheets of heterogenous catalysis biodiesel process using Aspen Plus 7.0 process simulator.

ii. Determine the potential environment impact (PEI) of biodiesel process using WAR algorithm method performed in spreadsheet of Microsoft Excel and comparing the results with homogeneous catalysis biodiesel process.

1.5 Significance of Proposed Study

The significance of this study is to provide another perspective of analyzing process design which is by taking account the environmental criteria. Analyzing of potential environmental impact (PEI) in process design improved the economic and environmental aspect of the process itself.

1.6 Thesis Structure

This thesis consist of five chapters which are, Introduction in the first chapter, Literature Review in chapter 2, Process Simulation in chapter 3, Environmental Analysis and Comparison in chapter 4, and Conclusion and Recommendation in chapter 5.

In this introduction chapter, background of proposed study, the problem statement, objectives, scopes and significance of proposed study are presented. As for the next chapter on Literature Review, previous study from researchers related with biodiesel productions and technologies, process synthesis of heterogeneous process, and environmental assessment of WAR algorithm are reviewed. In Chapter 3 on Process Simulation, parameters used for simulation process and the process design modeled are presented in details in this chapter. Simulation result is attached at the end of the chapter which is further used in Chapter 4 for environmental assessment.

Chapter 4 on Environmental Analysis and comparison discussed and compared the results of four PEI indexes and eight PEI categories within homogeneous and heterogenous process. Chapter 5 concluded the findings of this study and discussed points on improvement of the study. In overall, this study can be summarized as below:

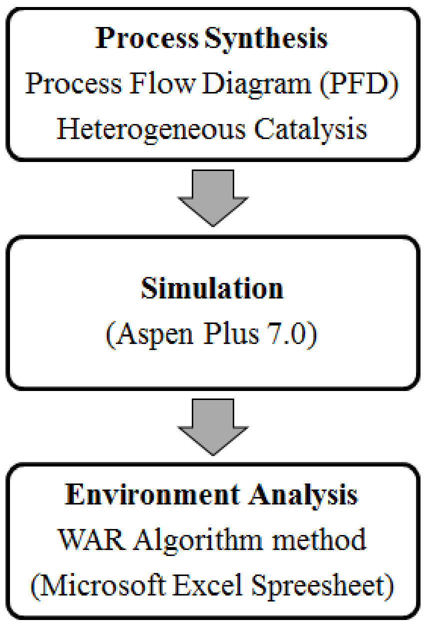

Figure 1.1 Schematic of the process design approach

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

In this chapter, background on the biodiesel and technical description on the heterogeneous catalysis biodiesel process are reviewed. Discussion on the environmental analysis using WAR algorithm method is reviewed.

2.2 Biodiesel

Biodiesel is a renewable energy produced by a catalyzed transesterification reaction of alcohol and natural triglycerides from vegetables oil or animal fats. The decreasing of fossil fuel supplies, the increasing of petroleum price, and the community concern on the environmental and human health impact from the uses of petroleum fuel do encourage the research and development on biodiesel.

Biodiesel is derived from vegetable oil or animal fat, a renewable, domestic resource which reduce the reliance on petroleum. The properties of biodiesel make it safe and useful for transportation. (West *et al*., 2008; Zhang *et al*., 2002). As biodiesel is biodegradable and non-toxic, it is suitably applied for transportation in highly sensitive environments while the high flash point of biodiesel (approximately 150 °C) compared to petroleum diesel which is around 50°C making it safe for transportation or when handling it because it is less volatile (Zhang *et al*., 2002). Biodiesel also improve the performance of engine exhaust emission by reducing the lifecycle of carbon dioxide emissions by 78% compared to diesel fuel engine. Reduction in carbon monoxide emission by 66.7%, particulate matter by 66.7%, unburned hydrocarbon by 45.2% and almost no sulfur or aromatic compound compared to petroleum diesel (West *et al*., 2008).

2.2.1 Biodiesel Production

Zhang *et al*., (2002) briefly described on four potential ways to reduce the viscosity of vegetable oil for the production of biodiesel which are: dilution, pyrolysis, microemulsion and transesterification. Transesterification reduced the molecular weight of oil, thus reducing the viscosity making it the best method for biodiesel production process which is therefore use in this study.

Several commercial processes to produce biodiesel have been developed and they are commercially produced in Europe and United States. In Europe, Austria, Italy, Germany and France commercially used biodiesel since 1988 with Germany as the largest biodiesel producer in Europe with total production capacity of 1.060.000 tons, followed by France with 520.000 tons in 2004 (Othman, 2011).

One limitation of large-scale commercialization is because of the high production cost (Zhang *et al.*, 2002; West *et al.*, 2008; Othman, 2011). West *et al*, (2008) suggested three methods in reducing the production cost which is first by replacing a virgin oil feedstock with a waste cooking oil feedstock. The second method is by the uses of alcohol in its supercritical state avoiding the uses of catalyst. The last method is by the uses of solid heterogeneous catalyst replacing the conventional liquid catalyst. In his study, production of biodiesel via continuous transesterification process using waste cooking oil as the feedstock and heterogeneous acid catalyst is concluded to have advantageous over the other processes with simple process design and much economically. Thus, the same technology in producing biodiesel will be focus in this study.

2.3 Process Description

2.3.1 Transesterification Technology

Transesterification reaction is the reaction within triglycerides from vegetables oil or animal fats with alkyl alcohol in the presence of catalyst to produce alkyl esters and glycerol. Recommended alcohols are those with low carbon chain such as methanol, ethanol and butanol. Methanol is commonly used, having fatty acid methyl esters (FAME or biodiesel) as the product and glycerol as the byproduct.

While for the feedstock, vegetable and animal fat such as soybean oil, canola oil, rapeseed oil, sunflower oil and beef tallow are commonly used (Zhang, 2002). Besides, the uses of low cost feedstock such as waste cooking oil may be adopted to reduce the production cost.

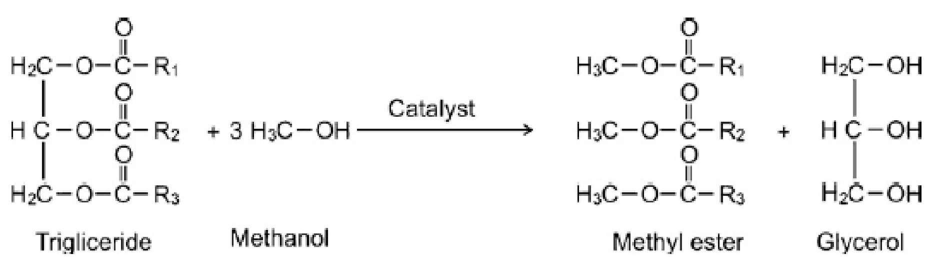

Figure 2.1 Biodiesel reaction
(Source: Chouhan & Sarma, 2011)

Since the reaction is not fast enough at low temperature, catalyst is use to fasten up the reaction. The catalyst can be an alkali, acid or enzyme either in liquid (homogeneous) or solid (heterogeneous) form. Common homogeneous catalyst used are sodium hydroxide, potassium hydroxide and sulfuric acid while for heterogeneous catalyst, metal oxide such as zinc oxide are frequently used. Due to the expensive processing stages of homogenous catalysis, heterogeneous catalysis is preferable.

From figure 2.1, the reaction required 3:1 molar alcohol to oil ratio, minimum ratio for the transesterification reaction to take place. However, excess alcohol is usually added to achieve higher ester yield (Dimian & Bildea, 2008; West *et al*., 2008; Othman, 2011). As for the condition of the reaction, it is normally run at temperature closed to the boiling point of alcohol and pressure slightly above the atmosphere pressure.

2.3.2 Heterogeneous Catalysis System

Heterogeneous catalytic transesterification is classified as green technology because the catalyst can be recycle, less amount of waste water is produce during the process, and ease separation of biodiesel from glycerol (Chouhan & Sarma, 2011). Heterogeneous catalysis process eliminated the purification step of catalyst and avoided the side reaction within free fatty acid and base alcohol therefore reducing the production cost of biodiesel (Othman, 2011).

Othman, (2011) had reviewed on the study by Furuta et al. in 2004 whereby in their study, they used solid superacid catalysis, tungstated zirconia, sulfated tin oxide and sulfated zirconia catalyst in the reaction. Various types of heterogeneous catalysts have been used for lab scale biodiesel production. Detailed reviewed and discussion on this is presented by Chouhan and Sarma, (2011).

In this study, biodiesel process is based on the study done by West *et al*., (2007). Basic heterogeneous catalysis biodiesel process includes transesterification reaction in the stoichiometric reactor, methanol recovery by the distillation column, glycerol separation through decanter and biodiesel purification in the distillation column.

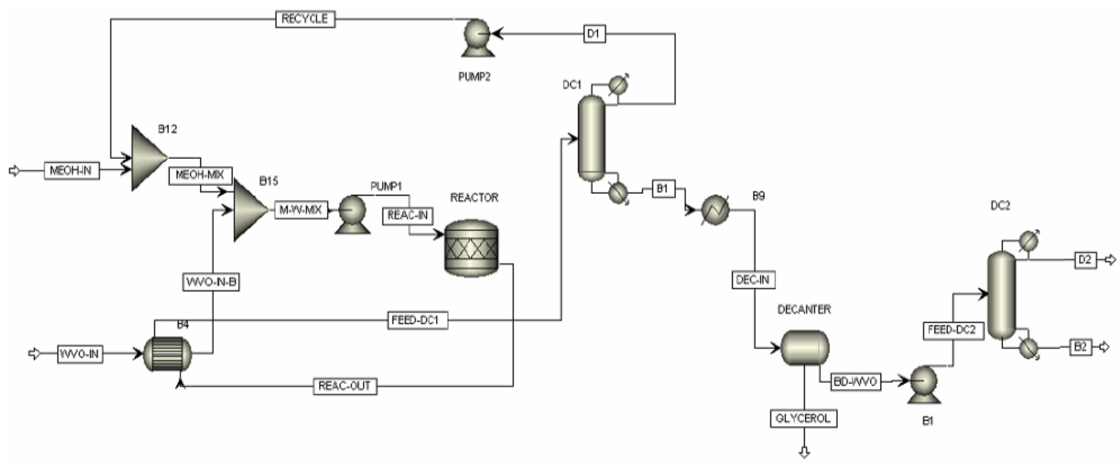

Figure 2.2 Heterogeneous acid-catalyzed process flowsheet
(Source: West *et al*., 2007)

2.4 Environmental Analysis using WAR Algorithm

Environmental assessment is important in a process plant in order to minimize the potential impact of hazardous chemical from process towards the environment. In designing a chemical process, pollution prevention technique is implemented into the process due to the environmental concerns. Young *et al.*, (2000) reviewed on the first implementation of pollution prevention which are via heat exchange networks (HENs) and mass exchange networks (MENs) in 1970s. While HENs focusing on reduction of energy consumption during manufacturing process, MENs concerning on reduction of waste generated from a process that require treatments. Waste reduction (WAR) algorithm is introduced by Hilaly and Sikdar (1994) to evaluate the environmental impact of the waste from chemical process. WAR algorithm originally introduced the concept of pollution balance, a methodology that allowed pollutants to be tracked throughout the process (Young *et al.*, 1999).

Generalized WAR algorithm with a potential environmental impact (PEI) is then introduced by Cabezas *et al.*, (1997) in order to consider the impact of the pollution generated within a process. While pollution balance tracked the pollutants, PEI balance quantifies the impact that indicates either the process is environmental friendliness or not (Young *et al.*, 1999).

Different methodologies may be applied as reviewed by Young *et al.,* (2000). However, WAR algorithm will be used to assess environmental performance of process design in this paper. This is because of the simple approaches it takes in describing and analyzing the environmental impact of the input-output material and energy stream in a process. The uses of simple algorithms as well as easy to find parameters making this method is preferable in analyzing the environmentally friendliness of chemicals in process towards the environment.

WAR algorithm is a tool used in evaluating the relative environmental impact of a chemical process. It is a methodology that only considers during the manufacturing process by not taking accounts the overall life cycle analysis (LCA). Thus, WAR algorithm is suitably used during the design stage of a new process or for modification of existent process design. Brief reviewed and comparison within LCA and WAR algorithm is presented by Othman, (2011).

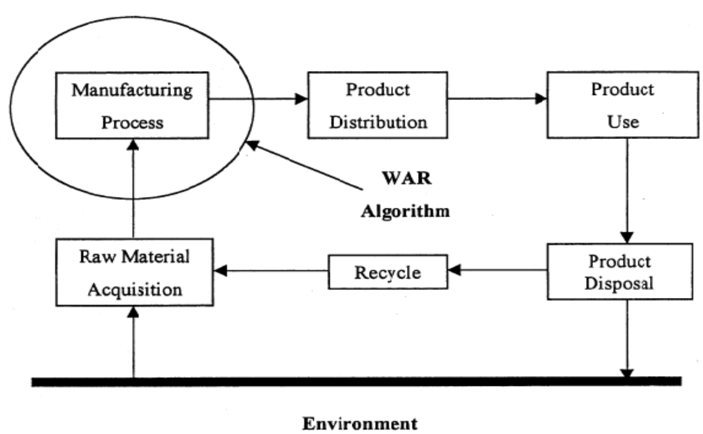

Figure 2.3 Product Life Cycle
WAR algorithm is performed during manufacturing process.
(Source: Young & Cabezas, 1999)